

PERIODIC BOUNDARY CONDITIONS FOR LONG-TIME NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS OF INCOMPRESSIBLE FLOWS

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ABSTRACT. This work presents a generalization of the Kraynik-Reinelt (KR) boundary conditions for nonequilibrium molecular dynamics simulations. In the simulation of steady, homogeneous flows with periodic boundary conditions, the simulation box moves with the flow, and it is possible for particle replicas to become arbitrarily close, causing a breakdown in the simulation. The KR boundary conditions avoid this problem for planar elongational flow and general planar mixed flow [J. Chem. Phys **133**, 14116 (2010)] through careful choice of the initial simulation box and by periodically remapping the simulation box in a way that conserves replica locations. In this work, the ideas are extended to a large class of three dimensional flows by using multiple remappings for the simulation box. The simulation box geometry is no longer time-periodic (which was shown to be impossible for uniaxial and biaxial stretching flows in the original work by Kraynik and Reinelt [Int. J. Multiphase Flow **18**, 1045 (1992)]). The presented algorithm applies to all flows with nondefective flow matrices, and in particular, to uniaxial and biaxial flows.

1. INTRODUCTION

Nonequilibrium molecular dynamics techniques are widely employed in the study of molecular fluids under steady flow. Periodic boundary conditions (PBCs) are employed to study bulk properties of a fluid, but standard PBCs with a fixed simulation box are incompatible with a homogeneous linear background flow $A = \nabla u \in \mathbb{R}^{3 \times 3}$, such as shear or elongational flow. In such a simulation, the periodic replicas of a particle have different velocities, consistent with the background flow. If we let

$$L_t = \begin{bmatrix} \mathbf{v}_t^1 & \mathbf{v}_t^2 & \mathbf{v}_t^3 \end{bmatrix} \in \mathbb{R}^{3 \times 3}, t \in [0, \infty)$$

denote the time-dependent lattice basis vectors defining the simulation box, then a particle with phase coordinates (\mathbf{Q}, \mathbf{V}) has periodic replicas with coordinates at $(\mathbf{Q} + L_t \mathbf{n}, \mathbf{V} + AL_t \mathbf{n})$ for all integer triples $\mathbf{n} \in \mathbb{Z}^3$. The velocity relations

$$\frac{d}{dt}(\mathbf{Q} + L_t \mathbf{n}) = \mathbf{V} + AL_t \mathbf{n} \text{ for all } \mathbf{n} \in \mathbb{Z}^3$$

imply that the simulation box must move with the flow,

$$\frac{d}{dt}L_t = AL_t, \text{ which has solution } L_t = e^{At}L_0. \quad (1)$$

For general flows, depending on the orientation of L_0 the simulation box can become quite elongated so that a particle is approached by its periodic replicas, which causes numerical instability in the simulation. For example, a planar elongational flow whose contraction is parallel to one of the simulation box edges \mathbf{v}_0^i has one periodic direction that shrinks exponentially fast. This puts a finite limit on the simulation stability [8, 1]. While these time periods are sometimes long enough to allow for the accurate computation of statistical observables in simple molecular fluids, there is need for boundary conditions without time limitations for the simulation of complex molecular systems.

For shear flow, the Lees-Edwards boundary conditions [11] allow for time-periodicity in the deforming simulation box itself. For planar elongational flow, the Kraynik-Reinelt (KR) boundary conditions [10, 14, 13, 2] achieve time periodicity in the simulation box by carefully choosing the vectors defining the initial simulation box. In particular, the box is rotated so that the edges form an angle of approximately 31.7 degrees

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with respect to the background flow. However, the KR formalism does not apply to general three dimensional flows, in particular it cannot treat uniaxial or biaxial flow [10]. In this paper, we generalize the KR boundary conditions to handle any homogeneous, incompressible, three-dimensional flow whose velocity gradient is a nondefective matrix (see Section 2 for a precise description of the flow types handled). We greatly enlarge the class of flows handled, including uniaxial and biaxial flows. The proposed algorithm gives an initial orientation for the lattice vectors L_0 , evolves the vectors according to the differential equation (1), and remaps the vectors in a fashion that preserves the periodic lattice structure and keeps the total deformation bounded for all time. Unlike Lees-Edwards and Kraynik-Reinelt boundary conditions, the boundary conditions do not in general have a time-periodic simulation box; however, the deformation of the simulation box is kept bounded and particle replicas stay separated by a bounded distance.

In Section 3 we review the KR boundary conditions and describe them in a framework useful for the generalization later. In Section 4 the new boundary conditions are derived and explained theoretically. Section 5 contains a self-contained description of the algorithm with default choices for parameters given.

We note that the boundary conditions described here are not tied to a particular choice of nonequilibrium dynamics. Typically, the flow in a nonequilibrium simulation is driven by a specialized dynamics, for example, the deterministic SLLOD [7, 4] or g-SLLOD [15, 5] dynamics or the nonequilibrium stochastic dynamics such as those in [12, 3].

2. FLOW TYPES AND AUTOMORPHISMS

Since the background flow treated here is incompressible, A is a trace-free matrix. Let $J = S^{-1}AS$ denote the real Jordan canonical form for A , where all 3 by 3 matrices fall in four possible cases,

$$J_1 = \begin{bmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & -\varepsilon_1 - \varepsilon_2 \end{bmatrix}, J_2 = \begin{bmatrix} \varepsilon & -r & 0 \\ r & \varepsilon & 0 \\ 0 & 0 & -2\varepsilon \end{bmatrix}, \quad (2)$$

$$J_3 = \begin{bmatrix} \varepsilon & 1 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & -2\varepsilon \end{bmatrix}, \text{ or } J_4 = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}. \quad (3)$$

The form J_1 includes several standard matrices, for example planar elongational flow (PEF) where $\varepsilon_1 = -\varepsilon_2$, uniaxial stretching flow (USF) where $\varepsilon_1 = \varepsilon_2 < 0$, and biaxial stretching flow (BSF) where $\varepsilon_1 = \varepsilon_2 > 0$. The matrix J_2 arises in the case of complex eigenvalues, corresponding to a rotational flow (which may be an inward spiral $a < 0$, an outward spiral $a > 0$, or a center $a = 0$). Both J_3 and J_4 are defective matrices, since they have rank-deficient eigenspaces. The generalized KR boundary conditions apply to any matrices of the form J_1 or J_2 . For J_3 , if $\varepsilon = 0$, then this is a case of planar shear flow and the Lees-Edwards boundary conditions can be employed. Likewise, similar boundary conditions can be employed for the case J_4 ; however, we have not been able to extend the boundary conditions described here to the J_3 case for nonzero ε .

In the following, we transform the lattice L_t with elements of $SL(3; \mathbb{Z})$, the matrix group of orientation-preserving linear lattice automorphisms. This is the set of all three by three matrices with integer entries whose determinant is 1. By Cramer's rule, such a matrix has an inverse with integer entries. For any $M \in SL(3; \mathbb{Z})$, the lattices generated by L_t and $L_t M$ are identical, and thus, the two sets of particles $\{\mathbf{Q}_i + L_t \mathbf{n} \mid \mathbf{n} \in \mathbb{Z}^3\}$ and $\{\mathbf{Q}_i + L_t M \mathbf{n} \mid \mathbf{n} \in \mathbb{Z}^3\}$ are identical. Applying such an automorphism transforms the simulation box without changing the simulated dynamics. Through the careful choice of initial simulation box L_0 and automorphisms, we can simulate a system where all particles maintain a minimum distance from their periodic replicas for all time.

3. KR BOUNDARY CONDITIONS AND PLANAR FLOWS

We first present a review of the KR boundary conditions for planar elongational flow along with a summary of techniques for other planar flows.

3.1. KR boundary conditions for planar elongational flow. Consider a diagonal flow of the form

$$A = \begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & -\varepsilon & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

where $\varepsilon > 0$.

The KR boundary conditions [10] consist in choosing a basis for the unit cell such that after a finite time, the elongational flow maps the lattice generated by the unit cell onto itself. That is, one finds a basis L and time $t_* > 0$ such that

$$e^{At_*}L = LM,$$

for some $M \in \text{SL}(3; \mathbb{Z})$. The mapping M is a parameter of the algorithm. The method was first described in [10], where the authors showed how to find reproducible square and hexagonal lattices in planar elongational flow. In [14, 2, 13] the authors employed these reproducible lattices in nonequilibrium molecular dynamics simulations by using them to describe the periodicity of groups of particles.

Choose $M \in \text{SL}(3; \mathbb{Z})$ with positive eigenvalues, other than the identity matrix. For example, the choice

$$M = \begin{bmatrix} 2 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

is common, and it has been shown to give a system with the largest possible minimal spacing between periodic replicas [10]. Let V denote a matrix of eigenvectors for M , and let

$$\Lambda = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda^{-1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

denote the matrix of corresponding eigenvalues, so that

$$MV = V\Lambda.$$

We order the eigenvalues so that $\lambda > 1$. The fact that the eigenvalues are inverses of one another follows from $\det(M) = 1$. We define the lattice time period

$$t_* = \frac{\log(\lambda)}{\varepsilon} \tag{4}$$

so that $e^{\varepsilon t_*} = \lambda$. Let $L_0 = V^{-1}$ be the matrix of initial lattice vectors. Note that while it is typical to choose eigenvectors to have norm one, the vectors in V should be scaled so that the unit cell $L_0 = V^{-1}$ has the desired volume for the simulation box. If one chooses the vectors of V to have the same length, then the vectors of V are orthogonal, and $V^{-1} = \frac{1}{\det(V)^2} V^T$. Since the lattice vectors move with the flow as in (1), at time t_* , they satisfy

$$L_{t_*} = e^{At_*}V^{-1} = \Lambda V^{-1} = L_0 M.$$

Thus, the lattice vectors L_{t_*} generate the same lattice as L_0 , demonstrating the time periodicity of the lattice. In simulations, the simulation box is remapped by setting

$$L_{t_*}^+ := L_0$$

to avoid the use of highly elongated basis vectors. This transformation does not move any of the periodic replicas of the particles in the simulation; however, since the basis vectors have changed, the periodic boundary conditions need to be applied on stored particle positions so that the stored particle displacements fall within the simulation box.

3.2. General planar flows. As mentioned in [10] and implemented for mixed flow in [9], the above algorithm can be applied to certain nondiagonal matrices A by diagonalization. However, in [10], it is shown by consideration of the characteristic polynomial for members of $SL(3; \mathbb{Z})$ that there is no reproducible lattice for either USF or BSF. Suppose now that A denotes a general incompressible planar flow, that is, all nonzero entries of the matrix act on a two-dimensional eigenspace. This corresponds to cases J_1 with $\varepsilon_1 = \varepsilon_2$, J_2 with $\varepsilon = 0$, or J_3 with $\varepsilon = 0$ in (2) and (3). There are three cases to consider, two nonzero real eigenvalues, two purely imaginary eigenvalues, or only zero eigenvalues.

3.2.1. Elongational flow. If the eigenvalues of A are real and distinct then A is diagonalizable and corresponds to an elongational flow. Let S denote a matrix of eigenvectors and D denote the matrix of eigenvalues for A so that $AS = SD$. Then, upon choosing the basis $L_0 = SV^{-1}$, we have

$$L_{t*} = e^{At*} L_0 = e^{At*} SV^{-1} = Se^{Dt*} V^{-1} = SV^{-1} M = L_0 M.$$

We note that this includes the mixed flow case treated in [9].

3.2.2. Rotational flow. In the case the eigenvalues are pure imaginary, and the flow is rotational. Writing A in real Jordan normal form, we choose real S so that

$$S^{-1}AS = \begin{bmatrix} 0 & r & 0 \\ -r & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

We define $L = S$ and then have that $e^{At}L = R_t L$, where R_t is a rotation for all t . There is no need to reset the simulation box in this case.

3.2.3. Shear flow. The final case of all zero eigenvalues corresponds to shear flow. We note that in this case, there is a t_* and S such that $e^{At_*}S = SM$, for

$$M = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

This is the Lagrangian rhomboid scheme, which is equivalent to the Lees-Edwards boundary conditions [11, 7].

4. GENERALIZED KR BOUNDARY CONDITIONS

In this section we generalize the boundary conditions to nondefective incompressible linear flows in three dimensions. In the following, rather than find a time t_0 such that $L_{t_0} = L_0 M$ for a single automorphism $M \in SL(3; \mathbb{Z})$, we consider the successive application of two different automorphisms $M_1, M_2 \in SL(3; \mathbb{Z})$ to L_t in order to keep the total deformation of the unit cell small for all times.

Suppose that $M_1, M_2 \in SL(3; \mathbb{Z})$ are a pair of commuting, symmetric automorphisms. Then the matrices are simultaneously diagonalizable by an orthogonal matrix V . Let

$$\Lambda_i = V^{-1} M_i V$$

denote the matrix of eigenvalues corresponding to M_i , whose diagonal entries are denoted by $\lambda_{i,1}, \lambda_{i,2}, \lambda_{i,3}$. We define the logarithm of the ordered spectrum for each operator

$$\hat{\omega}_i = \begin{bmatrix} \log \lambda_{i,1} \\ \log \lambda_{i,2} \\ \log \lambda_{i,3} \end{bmatrix} = \log \text{diag}(V^{-1} M_i V), \quad (5)$$

where $\text{diag}(M)$ denotes the column vector made up of the diagonal entries of the matrix M . We assume the following about M_1 and M_2 .

Assumption 4.1. *We assume that $M_1, M_2 \in SL(3; \mathbb{Z})$ are symmetric, commute, and have positive eigenvalues. We assume that $\hat{\omega}_1$ and $\hat{\omega}_2$, defined in (5), are linearly independent.*

An example of such a pair of matrices is given in Section 5. Note that the choice of M_1 and M_2 does not depend on the matrix A .

We describe the technique first in the diagonal case before discussing in turn the four possible cases for three dimensional flows. After the derivation given here, the main algorithm is presented in a concise form in Section 5.

4.1. Diagonal case. Let us first consider a diagonal flow of the form

$$A = \begin{bmatrix} \varepsilon_1 & & \\ & \varepsilon_2 & \\ & & \varepsilon_3 \end{bmatrix}, \quad (6)$$

where $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0$. Then the matrix exponential

$$e^{At} = \begin{bmatrix} e^{\varepsilon_1 t} & & \\ & e^{\varepsilon_2 t} & \\ & & e^{\varepsilon_3 t} \end{bmatrix}, \quad (7)$$

is diagonal for all time t .

Let M_1 and M_2 satisfy Assumption 4.1. We choose initial lattice basis $L_0 = V^{-1}$, where V diagonalizes M_1 and M_2 . Applying the transformation M_i to L_t gives

$$\begin{aligned} L_t M_i &= e^{At} V^{-1} M_i \\ &= \begin{bmatrix} e^{\varepsilon_1 t} & & \\ & e^{\varepsilon_2 t} & \\ & & e^{\varepsilon_3 t} \end{bmatrix} \begin{bmatrix} \lambda_{i,1} & & \\ & \lambda_{i,2} & \\ & & \lambda_{i,3} \end{bmatrix} V^{-1} \\ &= \exp \left(\begin{bmatrix} \varepsilon_1 t + \log \lambda_{i,1} & & \\ & \varepsilon_2 t + \log \lambda_{i,2} & \\ & & \varepsilon_3 t + \log \lambda_{i,3} \end{bmatrix} \right) V^{-1}. \end{aligned}$$

Similarly, if we apply multiple transformations at once, we have

$$L_t M_1^{n_1} M_2^{n_2} = \exp \left(\begin{bmatrix} \varepsilon_1 t & & \\ & \varepsilon_2 t & \\ & & \varepsilon_3 t \end{bmatrix} + \sum_{i=1}^2 n_i \begin{bmatrix} \log \lambda_{i,1} & & \\ & \log \lambda_{i,2} & \\ & & \log \lambda_{i,3} \end{bmatrix} \right) V^{-1} \quad (8)$$

where $n_1, n_2 \in \mathbb{Z}$. The idea of the algorithm presented in Section 5 is to apply automorphisms so that the argument of the exponential in (8) stays bounded for all times $t > 0$.

We define a vector that equals the diagonal part of the stretch,

$$\hat{\varepsilon}_t = \begin{bmatrix} \varepsilon_1 t \\ \varepsilon_2 t \\ \varepsilon_3 t \end{bmatrix},$$

and note that $\hat{\varepsilon}_t$, $\hat{\omega}_1$, and $\hat{\omega}_2$ belong to the two dimensional subspace $SS \subset \mathbb{R}^3$ of mean-zero vectors. The vectors $\hat{\omega}_1$ and $\hat{\omega}_2$ generate a lattice in SS ,

$$\mathcal{L} = \left\{ \left(n_1 - \frac{1}{2} \right) \hat{\omega}_1 + \left(n_2 - \frac{1}{2} \right) \hat{\omega}_2 \mid n_1, n_2 \in \mathbb{Z} \right\},$$

where we have added an offset of $1/2$ so that the unit cell

$$\hat{\Omega} = \left\{ \theta_1 \hat{\omega}_1 + \theta_2 \hat{\omega}_2 \mid \theta_1, \theta_2 \in \left(-\frac{1}{2}, \frac{1}{2} \right] \right\}$$

is centered at the origin. At each time $t > 0$, by applying powers of the automorphisms to the lattice, we can transform so that the remapped simulation box

$$\tilde{L}_t = L_t M_1^{n_1} M_2^{n_2}$$

has a small stretch vector $\tilde{\varepsilon}_t = \hat{\varepsilon}_t + n_1 \hat{\omega}_1 + n_2 \hat{\omega}_2$.

4.2. Diagonalizable flow. Suppose that A is diagonalizable,

$$A = SDS^{-1}.$$

As pointed out for the planar case in Section 3.2.1, we can extend the above algorithm, by choosing $L_0 = SV^{-1}$. We then have

$$L_t M_1^{n_1} M_2^{n_2} = e^{At} S V^{-1} M_1^{n_1} M_2^{n_2} = S e^{Dt} V^{-1} M_1^{n_1} M_2^{n_2}.$$

The automorphisms act to bound the stretch vector corresponding to the diagonal term e^{Dt} . We note that since S is not orthogonal if A is nonsymmetric, the original lattice vectors L_0 are not orthogonal in that case.

4.3. Complex eigenvalues. It is also possible that A has a pair of complex eigenvalues and a single real eigenvalue. We denote the spectrum of A as $\{\varepsilon + ir, \varepsilon - ir, -2\varepsilon\}$. In this case, we write the real Jordan normal form for the matrix,

$$A = S J_2 S^{-1},$$

where S is real and J_2 is the block-diagonal matrix

$$J_2 = \begin{bmatrix} \varepsilon & r & 0 \\ -r & \varepsilon & 0 \\ 0 & 0 & -2\varepsilon \end{bmatrix}.$$

We decompose $J_2 = D + B$ where

$$D = \begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & -2\varepsilon \end{bmatrix} \text{ and } B = \begin{bmatrix} 0 & r & 0 \\ -r & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

We note that since $DB = BD$, the matrix exponential splits into a rotation and a stretch giving

$$e^{At} = S e^{Jt} S^{-1} = S e^{Bt} e^{Dt} S^{-1},$$

where e^{Bt} is a rotation matrix. We again take initial lattice vectors $L_0 = SV^{-1}$ and control size of the stretch vector

$$\widehat{\varepsilon}_t = \begin{bmatrix} \varepsilon t \\ \varepsilon t \\ -2\varepsilon t \end{bmatrix},$$

using the automorphisms M_1 and M_2 . No effort is made to undo the effect of e^{Bt} since it is simply a rotation.

4.4. Defective matrices. The final possible case is when A is a defective matrix, that is, it has a repeated eigenvalue whose eigenspace does not have full rank. In three dimensions, a defective matrix can only occur for a matrix with a real spectrum, and so the only possible Jordan forms, up to rearrangement of the blocks, are

$$J_3 = \begin{bmatrix} \varepsilon & 1 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & -2\varepsilon \end{bmatrix} \text{ or } J_4 = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}.$$

We can treat the J_4 case very similarly to the shear flow case in Section 3.2.3, using the identity

$$e^{J_4 t} = \begin{bmatrix} 1 & t & \frac{t^2}{2} \\ 0 & 1 & t \\ 0 & 0 & 1 \end{bmatrix}.$$

We choose initial lattice basis $L_0 = S$ and note that at time $t_0 = 2$, we have

$$\begin{aligned} L_{t_0} &= e^{2A}S \\ &= Se^{2J_2} \\ &= S \begin{bmatrix} 1 & 2 & 2 \\ 0 & 1 & 2 \\ 0 & 0 & 1 \end{bmatrix} \\ &= SM, \end{aligned}$$

where $M \in \text{SL}(3; \mathbb{Z})$.

We have not been able to generalize our algorithm to the case of J_3 , when $\varepsilon \neq 0$. The difficulty lies with the off-diagonal terms of the matrix exponential

$$e^{J_3 t} = \begin{bmatrix} e^{\varepsilon t} & t e^{\varepsilon t} & 0 \\ 0 & e^{\varepsilon t} & 0 \\ 0 & 0 & e^{-2\varepsilon t} \end{bmatrix}.$$

One approach considered is to find matrices $M_j \in \text{SL}(3; \mathbb{Z})$ and a common matrix V such that $V^{-1}M_jV$ is upper triangular, in order to control the diagonal and off-diagonal terms at the same time, but we have not had success in such a construction.

5. ALGORITHM

We now provide an explicit construction of the generalized KR boundary conditions algorithm. The following two matrices are in $\text{SL}(3; \mathbb{Z})$ and they commute:

$$M_1 = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 2 & 2 \\ 1 & 2 & 3 \end{bmatrix} \quad M_2 = \begin{bmatrix} 2 & -2 & 1 \\ -2 & 3 & -1 \\ 1 & -1 & 1 \end{bmatrix}.$$

We choose the initial lattice vectors $L_0 = aV^{-1}$, where V denotes the matrix of eigenvectors for M_1 and M_2 , and a^3 is the volume of the simulation box. We fix the choice of ordering for the eigenvectors by giving the first few digits of V^{-1} ,

$$V^{-1} = \begin{bmatrix} 0.591 & -0.737 & 0.328 \\ 0.737 & 0.328 & -0.591 \\ 0.328 & 0.591 & 0.737 \end{bmatrix}$$

Direct computation shows that the ordered spectra of the two operators are positive and the corresponding $\hat{\omega}_i$, given by

$$\hat{\omega}_1 \approx \begin{bmatrix} -1.178 \\ 1.619 \\ -0.441 \end{bmatrix} \quad \hat{\omega}_2 \approx \begin{bmatrix} 1.619 \\ -0.441 \\ -1.178 \end{bmatrix}$$

are linearly independent.

Suppose that A is written in real Jordan normal form $A = SJS^{-1}$ and J is decomposed as $J = D + B$ where

$$D = \begin{bmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_1 & 0 \\ 0 & 0 & \varepsilon_3 \end{bmatrix} \quad \text{and} \quad B = \begin{bmatrix} 0 & r & 0 \\ -r & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

This encompasses both diagonalizable flow (where $B = 0$) and the case of complex eigenvalues, but does not include the defective matrix case (3).

For time $t \geq 0$, we define the reduced stretch $\tilde{\varepsilon}_t$ as follows

$$\frac{d}{dt} \tilde{\varepsilon}_t = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix}, \quad \tilde{\varepsilon}_0 = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix},$$

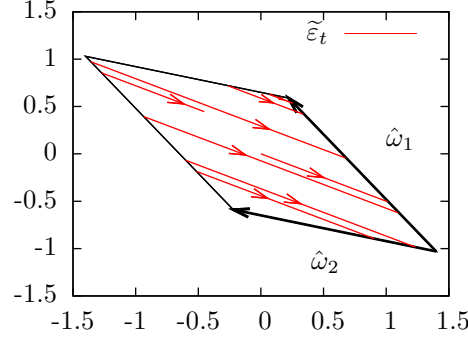


FIGURE 1. As the simulation progresses, $\tilde{\varepsilon}_t$ traces a curve in the unit cell $\hat{\Omega}$ within SS . Here, the unit cell $\hat{\Omega}$ of the lattice in stretch space has been projected into the xy plane. The lines within the parallelogram denote the evolution of $\tilde{\varepsilon}_t$ during a simulation of uniaxial stretching flow. The depicted unit cell corresponds to the example automorphisms given in Section 5.

where $\tilde{\varepsilon}_t$ is restricted to be within the unit cell

$$\hat{\Omega} = \left\{ \theta_1 \hat{\omega}_1 + \theta_2 \hat{\omega}_2 \mid \theta_1, \theta_2 \in \left(-\frac{1}{2}, \frac{1}{2} \right] \right\},$$

by periodic boundary conditions. An example curve $\tilde{\varepsilon}_t$ is depicted in Figure 1. The lattice basis vectors for the simulation are then defined to be

$$\tilde{L}_t = S e^{Bt} e^{\tilde{\varepsilon}_t} V^{-1},$$

where we define

$$e^{\tilde{\varepsilon}_t} = \exp \left(\begin{bmatrix} \tilde{\varepsilon}_{t,1} & & \\ & \tilde{\varepsilon}_{t,2} & \\ & & \tilde{\varepsilon}_{t,3} \end{bmatrix} \right).$$

This process can be carried out for arbitrarily long times, and the stretch $\tilde{\varepsilon}_t$ stays bounded for all times.

This gives the following pseudocode for the discretized version of the NEMD system: Given S, D, B , and the time step Δt , compute (δ_1, δ_2) so that $\delta_1 \hat{\omega}_1 + \delta_2 \hat{\omega}_2 = [\varepsilon_1, \varepsilon_2, \varepsilon_3]^T$. For each time step do:

- (1) $\theta_i \leftarrow \theta_i + \delta_i \Delta t$
- (2) $\theta_i \leftarrow \theta_i - \text{round}(\theta_i)$
- (3) $\tilde{\varepsilon}_t \leftarrow \theta_1 \hat{\omega}_1 + \theta_2 \hat{\omega}_2$
- (4) $\tilde{L}_t \leftarrow S e^{Bt} e^{\tilde{\varepsilon}_t} V^{-1}$

Note that we recompute the lattice basis vectors at each step, and we do not explicitly apply automorphisms nor do we directly reset the lattice vectors.

5.1. Minimum replica distance. The boundary conditions above limit the stretch $\tilde{\varepsilon}_t$ to live within the unit cell $\hat{\Omega}$ which is defined by the vectors (5). The minimum distance between a particle and a periodic replica within the simulation is given by

$$d = \min_{\substack{\mathbf{n} \in \mathbb{Z}^3 \setminus \{0\} \\ t \in \mathbb{R}^{\geq 0}}} \|\mathbf{q}_i + \tilde{L}_t \mathbf{n} - \mathbf{q}_i\| \geq \min_{\substack{\mathbf{n} \in \mathbb{Z}^3 \setminus \{0\} \\ \tilde{\varepsilon} \in \hat{\Omega}}} \|S e^{\tilde{\varepsilon}} V^{-1} \mathbf{n}\|.$$

Using the boundedness of $\hat{\Omega}$, we can limit the search to a small number of $\mathbf{n} \in \mathbb{Z}^3$, and minimization over $\hat{\Omega}$ leaves a quick computation. For the matrices in Section 5, if the vectors of S are orthogonal, the minimum distance is $d \approx 0.8198a$, where we recall that a^3 is the volume of the simulation box.

6. NUMERICS

In the following, we test the consistency of our algorithm by comparing computations for a WCA fluid under three-dimensional elongation to those presented in [1]. In previous works, the simulation time was restricted by the elongation of the unit cell, though the authors in [1] proposed a doubling scheme that increased the size of the unit cell to increase the simulation time. This came at the tradeoff of additional computational cost. In the following, we show that our simulations using the generalized KR boundary conditions converge to the same macroscopic quantities even after several cell resets.

We use the WCA potential [16], which is given by

$$\phi(r) = \begin{cases} 4 \left[\frac{1}{r^{12}} - \frac{1}{r^6} \right] + 1, & r \leq 2^{1/6}, \\ 0, & r > 2^{1/6}. \end{cases}$$

We simulate $N = 512$ particles at the scaled temperature $T = 0.722$ and fluid density $\rho = 0.8442$. For consistency with previous works [1, 9], we employ the SLLOD equations of motion [6] with Gaussian (isokinetic) thermostat [7], which is given by

$$\begin{aligned} \frac{d\mathbf{q}}{dt} &= \mathbf{v}, \\ \frac{d\mathbf{v}}{dt} &= M^{-1}\mathbf{f} + A\mathbf{A}\mathbf{q} - \alpha(\mathbf{v} - A\mathbf{q}), \\ \alpha &= \frac{(M^{-1}\mathbf{f} - A\mathbf{v} + A\mathbf{A}\mathbf{q}) \cdot (\mathbf{v} - A\mathbf{q})}{(\mathbf{v} - A\mathbf{q}) \cdot (\mathbf{v} - A\mathbf{q})}, \end{aligned}$$

where $\mathbf{q} \in \mathbb{R}^{3N}$ denotes the vector of all particle positions, $\mathbf{v} \in \mathbb{R}^{3N}$ denotes the corresponding velocities, and $\mathbf{f} \in \mathbb{R}^{3N}$ denotes the interaction forces on the particles. The factor α ensures that the relative kinetic energy $\frac{1}{2}(\mathbf{v} - A\mathbf{q})^2$ is exactly preserved by the dynamics.

We run our simulations up to time $t_{\max} = 20$, with time step $\Delta t = 0.002$. The initial positions are on a lattice with random velocities that are scaled so the system has the temperature $T = 0.722$. We allow a decorrelation step from the initial conditions up to time $t = 2$, and then average the desired observables until t_{\max} . For the largest strains, the unit cell is remapped approximately 15 times over the course of the simulation. We run ten realizations for each type of flow. We compute the virial stress tensor,

$$\sigma = -\frac{1}{\det L_t} \sum_{i=1}^N \left(M(\mathbf{v}_i - A\mathbf{q}_i) \otimes (\mathbf{v}_i - A\mathbf{q}_i) + \frac{1}{2} \sum_{\substack{i,j=1 \\ j \neq i}}^N (\mathbf{q}_i - \mathbf{q}_j) \otimes f^{(ij)} \right) \quad (9)$$

where

$$f^{(ij)} = -\phi'(|\mathbf{q}_i - \mathbf{q}_j|) \frac{\mathbf{q}_i - \mathbf{q}_j}{|\mathbf{q}_i - \mathbf{q}_j|}.$$

We also use the pressure tensor, $P = -\sigma$. In Figure 2, we plot the pressures for three different elongational flow types, planar elongational flow (PEF), uniaxial stretching flow (USF), and biaxial stretching flow (BSF), which have the respective velocity gradients

$$A_{PEF} = \begin{bmatrix} \varepsilon & & \\ & -\varepsilon & \\ & & 0 \end{bmatrix} \quad A_{USF} = \begin{bmatrix} \varepsilon & & \\ & -\varepsilon/2 & \\ & & -\varepsilon/2 \end{bmatrix} \quad A_{BSF} = \begin{bmatrix} -\varepsilon & & \\ & \varepsilon/2 & \\ & & \varepsilon/2 \end{bmatrix}$$

where $\varepsilon > 0$. In Figure 2(a) the pressure in the extensional direction is plotted versus ε , and in Figure 2(b) the pressure in the compression direction is plotted versus ε . These plots show close agreement to the plots [1, Fig. 8 and Fig. 9].

For a given velocity gradient A , we define $\gamma = A + A^T$, and define the generalized viscosity [8]

$$\eta = \frac{\sigma : \gamma}{\gamma : \gamma},$$

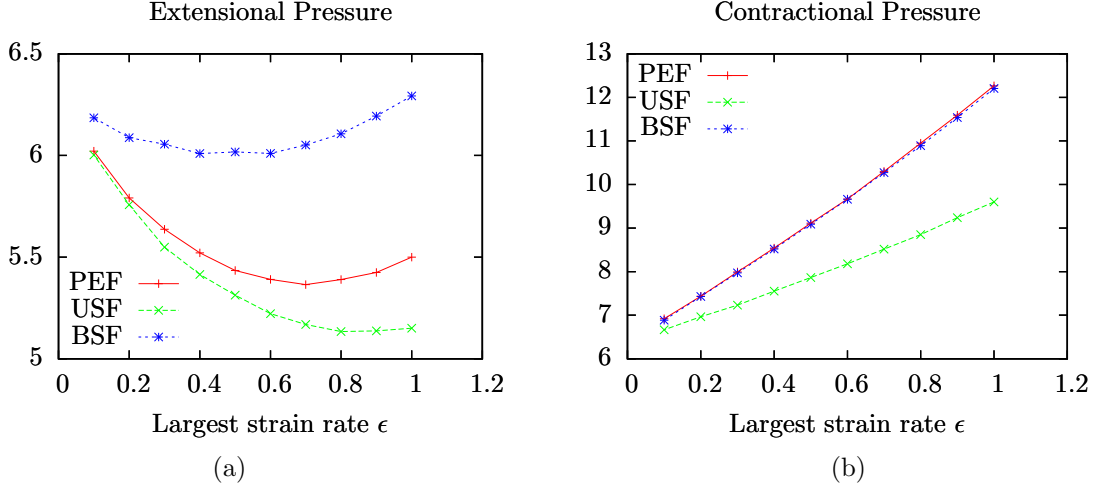


FIGURE 2. Pressures for PEF, USF, and BSF flows. Components of the pressure tensor (which is the negative stress (9)) are plotted against the largest magnitude component of the velocity gradient tensor. In (a) the pressure in the direction of extension is plotted, while in (b) the pressure in the direction of contraction is plotted. These plots show close agreement to the plots [1, Fig. 8 and Fig. 9].

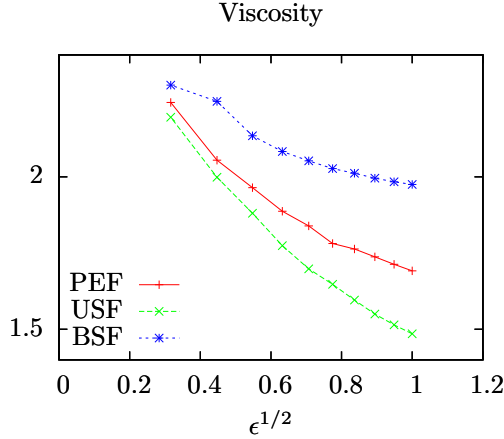


FIGURE 3. Viscosity for PEF, USF, and BSF flows. These plots show close agreement to the plots [1, Fig. 6].

where $A : B = \sum_{i,j} A_{ij} B_{ij}$ denotes the contraction product of a pair of tensors. In Figure 3 we plot the viscosity against the square root of ϵ .

Remark 6.1. We note that the WCA fluid we simulate is a simple fluid, with short decorrelation time, so that it is possible to use finite duration simulations. Our algorithm has more practical application for complex molecular systems where the decorrelation time is longer than allowed by traditional, time-restricted simulations. The above numerics are to show consistency of the computational results in a simple case.

7. CONCLUSION

We have generalized the KR boundary conditions to handle all homogeneous, incompressible three dimensional flows whose velocity gradient is a nondefective matrix. In particular, it can treat the cases of uniaxial or biaxial flow, which could not be treated with the original KR boundary conditions. The boundary conditions allow the simulations to continue for arbitrarily long times, which is important for the simulation of complex fluids with large decorrelation times.

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